EPR studies on an “unperturbed” CrO$_4^{2-}$ center in K$_2$SO$_4$ crystals

Y. Ravi Sekhar and H. Bill
Groupe de Physico-Chimie du Solide, Université de Genève, 30, Quai E. Ansermet, 1211 Geneva 4, Switzerland

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Electron paramagnetic resonance of CrO$_4^{2-}$ doped K$_2$SO$_4$ crystals has been studied after x-irradiation at 77 K. The resulting species, a CrO$_4^{2-}$ center, has the principal $g$ values $g_x = 1.8743$, $g_y = 1.8507$, and $g_z = 1.9386$. The EPR data indicate a small distortion of CrO$_4^{2-}$ tetrahedra. A temperature variation study of the spectra in the range 1.6–77 K shows that they broaden rapidly above 10 K and no motionally averaged spectrum is observed. The experimental results are discussed in terms of several effects including a possible Jahn–Teller effect.

The nature of the ground state and electronic structure of CrO$_4^{2-}$ and MnO$_4^{2-}$ ions have attracted considerable attention in recent years. The unpaired electron responsible for the EPR in these clusters was found to occupy a $d_z^2$ or $d_{xy}$ ground state depending on the lattice and the distortion of the host XO$_4^{2-}$ ion from ideal $T_d$ symmetry. In our previous investigations, we have attempted to study and compare CrO$_4^{2-}$ and MnO$_4^{2-}$ ions in the same lattice (namely K$_2$SO$_4$) in order to obtain a consistent basis to establish the electronic structure in their ground state. The CrO$_4^{2-}$ doped K$_2$SO$_4$ were x-irradiated at 300 K to produce CrO$_4^{2-}$ ions and their EPR was studied. It turned out that the results obtained on the CrO$_4^{2-}$ were quite different (with respect to the $g$ values, and their orientation) from those obtained in MnO$_4^{2-}$ doped K$_2$SO$_4$ crystals. This different behavior was attributed to the presence of a nearby proton (produced by RT irradiation) as evidenced by ENDOR measurements. In the present paper, we report on a CrO$_4^{2-}$ center which does not seem to have any nearby lattice defect or impurity associated. We have succeeded in creating this center by irradiating the crystals at 77 K.

Single crystals of K$_2$SO$_4$:CrO$_4^{2-}$ have been grown by slow evaporation of aqueous solutions. The presence of the CrO$_4^{2-}$ impurity has been checked by optical and Raman spectroscopies. The unpolarized Raman lines were observed at $v_h(A_1)$: 865 cm$^{-1}$, $v_2(E)$: 354 cm$^{-1}$, $v_3(T_2)$: 390, 394, 399 cm$^{-1}$, and $v_4(T_2)$: 900, 906, 925 cm$^{-1}$. The as-grown crystals did not show any EPR lines. They were then irradiated at 77 K using a Philips x-ray generator at 40 kV and 40 mA for about 24 h. No new EPR lines associated with CrO$_4^{2-}$ were found at 77 K while well defined resonances could be seen at 4.2 K. A temperature variation study showed that these EPR lines broaden rapidly above 10 K and were not detectable above about 18 K.

Figure 1 shows the experimental spectra along the $c$ axis. The hyperfine lines from the 9.5% abundant $^{52}$Cr ($I = 3/2$) are clearly seen only along this direction. The low field lines at $g = 2.0423$ and $g = 2.0094$ in Fig. 1 are readily identified as due to SO$_2$ and SO$_2^-$ radicals respectively, resulting from the damage of the host SO$_2^-$ ions. The angular variation of the $g$ values has been studied in the three crystallographic planes and are depicted in Fig. 2. When the magnetic field is rotated in an $(a, b)$ or $(a, c)$ plane, a single line is seen while in the $(b, c)$ plane (the mirror plane of the crystal), two lines appear except along the $b$ and $c$ axes. K$_2$SO$_4$ crystals belong to the orthorhombic space group $D_{2h}^7$ (at RT) with four sulphate ions per unit cell. These four ions can be divided into two pairs where members of a pair are related by reflection in the $(a, b)$ and $(a, c)$ planes. The SO$_2^-$ ions in the K$_2$SO$_4$ lattice occupy sites of $C_s$ symmetry. The observed angular dependence of the spectra agrees with a $C_s$ site symmetry of the CrO$_4^{2-}$ ion. Note that CrO$_4^{2-}$ ion has one unpaired electron ($S = 1/2$).

![Figure 1](https://example.com/figure1.png)

**FIG. 1.** $X$-band EPR spectrum of CrO$_4^{2-}$ doped K$_2$SO$_4$ crystals along $c$ axis at 4.2 K after x irradiation at 77 K. The $^{52}$Cr hyperfine components are indicated by the stick diagram below.
Experimentally, we have the following situation: when the crystals are irradiated at 300 K, the main species of the damage is the CrO$_2$\(^{2-}\) center with a nearby proton. The CrO$_2$\(^{2-}\) center without any associated defect is also produced under these conditions but with a much lower yield. On the other hand, when the crystals are irradiated at 77 K, the presently reported CrO$_2$\(^{2-}\) centers seem to form more efficiently than those associated with protons. We have indeed observed comparable concentrations of these two different centers in a number of crystals. Figure 3 summarizes these observations.

The principal g values of the presently reported CrO$_2$\(^{2-}\) center are given in Table I along with the earlier data on relevant systems. The C$_3$ symmetry of the molecule requires that one of the principal g values, designated as $g_x$ here, is along the a axis (direction perpendicular to the mirror plane). The other two, $g_y$ and $g_z$, lie in the mirror plane (b, c). We can now compare our results with those obtained on MnO$_2$\(^{2-}\) in K$_2$SO$_4$ and K$_2$CrO$_3$ crystals earlier.\(^{3,4}\) In order to unify the different results, the orientation of the g tensor in the mirror plane is represented geometrically in Fig. 4 in each of these cases. Note that the EPR experiments do not allow us to distinguish between the two possible orientations of the g tensor in the mirror plane ($g_y, g_z$ and $g_y', g_z$). However, we notice from Table I and Fig. 4 that CrO$_2$\(^{2-}\) in K$_2$SO$_4$ has a predominantly $d_{2z}$ ground state as ($g_x - g_y), (g_x - g_z) > (g_x - g_z)$ where $g_x = 2.0023$.

The $^{53}$Cr hyperfine lines could be resolved at only a few orientations owing to (i) the angular dependent line widths and (ii) the presence of weak lines from other centers. As can be seen from Fig. 1 and Fig. 3, the main EPR line has a width of about 4 G along c axis ($g = 1.9289$) and broadens up to about 28 G along other orientations. These facts coupled with the low intensity of the $^{53}$Cr EPR lines precluded us from making a complete analysis of the hyperfine data. However, from the plots of $A^2g^2 = A^2g^2[\cos^2(\theta - \theta_0)]$, an approximate estimation of the principal $A$ values was obtained. These are $A_x = 36$, $A_y = 30$, and $A_z = 8 \times 10^{-4}$ cm$^{-1}$ and $\theta_0 \approx 25^\circ$. Here, $A_x$ is parallel to the a axis of the crystal and $A_y, A_z$ are oriented in the bc plane. The noncoincidence of the g and A tensors has been observed in many of the CrO$_2$\(^{2-}\) and MnO$_2$\(^{2-}\) doped systems studied earlier\(^{6}\) and is associated with the molecular nature of these centers. A comparison of the present results with those obtained in CrO$_2$\(^{2-}\) doped Li$_2$PO$_4$ crystals\(^{3}\) shows that $A_x, A_y$, and $A_z$ are in the same order of magnitude in the two cases. It may be remarked that the hyperfine structure data in the latter case are also complicated by the line broadening and no consistent fitting could be achieved. Thus, these data remain very tentative in view of the uncertainty in the measurements.

<table>
<thead>
<tr>
<th>System</th>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
<th>Approximate ground state</th>
<th>Ref.</th>
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</thead>
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<tr>
<td>K$_2$SO$_4$: CrO$_2$(^{2-})</td>
<td>1.8743</td>
<td>1.8507</td>
<td>1.9386</td>
<td>$d_\rho$</td>
<td>Present work</td>
</tr>
<tr>
<td>Li$_2$PO$_4$: CrO$_2$(^{2-})</td>
<td>1.7411</td>
<td>1.7722</td>
<td>1.9402</td>
<td>$d_\rho$</td>
<td>3</td>
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<tr>
<td>K$_2$SO$_4$: MnO$_2$(^{2-})</td>
<td>1.9696</td>
<td>1.9757</td>
<td>1.9445</td>
<td>$d_{2z}$</td>
<td>2</td>
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<tr>
<td>K$_2$CrO$_3$: MnO$_2$(^{2-})</td>
<td>1.970</td>
<td>1.966</td>
<td>1.938</td>
<td>$d_{2z}$</td>
<td>8</td>
</tr>
</tbody>
</table>

FIG. 2. The angular variation in the three crystallographic planes of the line at $g = 1.9289$ in Fig. 1. (i) (b, c) plane (with b axis at $\Theta = 0^\circ$); (ii) (a, c) plane (with a axis at $\Theta = 0^\circ$); (iii) (a, b) plane (with b axis at $\theta = 0^\circ$).

FIG. 3. Comparison of the two CrO$_2$\(^{2-}\) centers produced in K$_2$SO$_4$:CrO$_2$\(^{2-}\) crystals. The EPR spectra shown are taken along the a axis under identical conditions. (i) Spectrum at 4.2 K after x irradiation at 77 K identified as due to CrO$_2$\(^{2-}\) without any associated defect. (ii) Spectrum at 4.2 K after irradiation at 300 K. The lines marked as $A_1$ and $A_2$ have been discussed earlier in Ref. 6 and identified as due to CrO$_2$\(^{2-}\) with a nearby proton.
values, their order and orientation in the mirror plane. Another common feature is the temperature dependence. Both exhibit EPR only below about 25 K. The CrO$_4^{2-}$ introduced into Li$_3$PO$_4$ host also has particularly large $\Delta g$ values. Li$_3$PO$_4$ is a remarkable host in the sense that the PO$_4^{3-}$ ions are very nearly tetrahedral, although it belongs to the same space group as K$_3$SO$_4$ crystals. The comparison between our results and those obtained in Li$_3$PO$_4$ seems to us quite valuable. It shows that an adequate description of the ground state of XO$_4^{2-}$ centers has to involve a consideration of several effects which are probably in a rather delicate mutual balance. Indeed, there is a possibility of a $E \otimes \epsilon$ (tetragonal) type molecular Jahn–Teller effect, or a trigonal $E \otimes \epsilon$ molecular JT effect, together with the low symmetry lattice ligand field. It is well known, based on the angular overlap model, that tetrahedral (tetragonal) $E \otimes \epsilon$ $d^1$ systems imply rather small JT coupling constants whereas the trigonal JT effect involves stronger ones. But, this latter effect goes through an admixture of excited states (via the trigonal part essentially of the intramolecular ligand field) which transform as $T_2$ in tetrahedral symmetry. In addition, the intermolecular ligand field in these hosts is not very strong as is shown by the short relaxation times. Thus, it is likely that all the three effects discussed above are to be considered simultaneously (eventually in part in the form of a pseudo-Jahn–Teller effect), because a straightforward application of the crystal field model leads to quite inconsistent conclusions. This fact is supported by the noncoincident orientations of $g$ and $3A^1$ indicating important $s$, $p$ oxygen contribution to the ground state wave function of the molecular ion.

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